



SECRET

SECRET

50X1-HUM

Hydrogen compounds of elements of the fourth group are unable to form onium compounds with ions of hydrogen because free electron pairs are absent. Hydrogen compounds of elements of the fourth group also have no tendency, as a rule, to dissociate with the formation of hydrogen ions, and, therefore, hydrogen cannot be exchanged with other hydrogen compounds, even those which easily form onium complexes.

However, in certain cases the exchange will take place. As G. P. Miklukhin (2) succeeded in proving, the exchange will take place when substituents which are capable of attracting electrons to themselves are present in a hydrogen compound of carbon. This phenomenon facilitates the formation of onium complexes and, consequently, the exchange of hydrogen.

By means of investigations with the aid of a radioactive isotope of bromine, N. Ye. Brezhneva, S. Z. Roginskiy, and A. I. Shilinskiy (3) obtained extremely interesting data on the variable activity of the bonds between carbon and bromine. It was shown, for example, that the bond between bromine and carbon found in a hydrocarbon chain is considerably more active than the bond between bromine and carbon in the benzene ring.

With the aid of a radioactive isotope of sulfur, a divergence in the properties of the two sulfur atoms was proven in the ion  $S_2O_3^{--}$ . The "external" sulfur of the ion  $S_2O_3^{--}$  is closer to the atomic state than to the state of the ion S -- (4).

We made an attempt to investigate the variation of the properties of bonds to bromine by means of the exchange of one element for another in the same subgroup of the periodic system. Employing a radioactive isotope of bromine to study isotopic exchange reactions, we succeeded in obtaining certain new data which describe properties of bonds between these elements and bromine. We investigated the exchange reactions of bromine in the systems bromine-tetrabromides of fourth group elements (carbon, silicon, and tin).

The exchange reactions were conducted in sealed tubes. The bromide was placed in the tubes, liquid bromine added, and the tube sealed. The liquid bromine was marked by an admixture of the radioactive isotope of bromine. The quantities of liquid bromine and bromide were so calculated that there would be an identical quantity of bromine atoms in each. The sealed tube was kept for a certain time at a specified temperature under thermostatically controlled conditions. Then cooled tube was opened and the free bromine removed either by suction or by passing a current of dry  $CO_2$  over it. Both the free bromide and the bromine which composed the tetrabromide were converted into silver bromide. Precipitates of silver bromide were isolated for the measurement of activity. The results of the measurements are presented in Table 1

At room temperature there was no noticeable exchange of bromine between the carbon tetrabromide and the liquid bromine. At  $100^\circ$  there was discovered a weak exchange of bromine, amounting to about 10% of complete exchange. These data are found to be in agreement with earlier investigations of this system (5).

In the silicon tetrabromide-bromide system no exchange of bromine was discovered at either  $20^\circ$  or  $100^\circ$ .

The tetrabromide of tin exchanged its bromine easily and completely even at  $20^\circ$ .

These results indicate a significant difference in the course of the isotopic exchange reactions of bromine in the enumerated systems. However, the difference between the carbon tetrabromide and the silicon tetrabromide is not sufficiently clear.

- 2 -

SECRET

SECRET

SECRET

SECRET

50X1-HUM

We proposed to obtain new data which would characterize the properties of the bonds of carbon and silicon with bromine through the study of the exchange reactions of bromine between the tetrabromides of these elements and aluminum bromide.

As is known, molecules of aluminum bromide have a tendency to form complex compounds with the compounds with the coordination number 4 for aluminum. A large number of complex compounds of aluminum bromide with various inorganic and organic substances is known (6,7).

In complex compounds, aluminum bromide shows definite polarizability, according to the data obtained by I. A. Sheka (8) through the measurement of the dipole moments of aluminum bromide in its compounds with various organic substances.

A series of phenomena brought about by the activating effect of aluminum bromide in its complex compounds containing certain substances has been pointed out (7). These properties of aluminum bromide show, as one might expect, that the process of exchange will take place much more easily with aluminum bromide than with free bromine. This is also pointed out by the data obtained by Brezhneva, Roginskiy, and Shilinskiy (3), from which it follows that aluminum bromide easily exchanges its bromine with certain organic bromine derivatives.

Addition to aluminum bromide renders unstable the bonds with bromine in the other bromine compound and facilitates the process of exchange. The exchange reactions between aluminum bromide and  $\text{CBr}_4$  or  $\text{SiBr}_4$  also were conducted in sealed tubes. Aluminum bromide containing a certain quantity of the radioactive isotope of bromine was placed in the tube, the tetrabromide being studied was added in an approximately equimolecular ratio, and the tube was sealed. The mixture was kept for a certain time in a thermostat after which the tube was opened and the components of the reaction were separated.

The silicon tetrabromide was separated from the aluminum bromide by distillation in vacuum. The carbon tetrabromide was separated from the aluminum bromide by distillation in vacuum or by treatment with a dilute solution of nitric acid.

The bromine contained in  $\text{AlBr}_3$ ,  $\text{CBr}_4$ , and  $\text{SiBr}_4$  was converted into silver bromide. Equal aliquot quantities of silver bromide were prepared for the measurement of activity. The results of the measurements are presented in Table 2.

As is evident from the data in Table 2, a complete exchange of bromine takes place in the  $\text{CBr}_4$ - $\text{AlBr}_3$  system. In contrast to this, the bonds with silicon in  $\text{SiBr}_4$  are so inactive that in the  $\text{SiBr}_4$ - $\text{AlBr}_3$  system no exchange of bromine could be discovered, just as in the  $\text{SiBr}_4$ -bromine system.

This striking difference of  $\text{SiBr}_4$  from  $\text{CBr}_4$  and  $\text{SnBr}_4$  in connection with reactions of the isotopic exchange of bromine may be explained by the combination of properties of these bromides and the structural peculiarities in their molecules.

Evidently one reason for such weak activity on the part of the bonds between bromine and silicon, in comparison with the bonds between bromine and carbon, is the possibility of the formation between silicon and bromine of partly double bonds as a result of the donor-acceptor relationship of silicon and bromine. As distinguished from carbon, silicon is limited by no strict octet rule and can also employ the d-orbits for the formation of bonds. Atoms of bromine, combined with silicon by ordinary covalent bonds, seem to be donors of electrons in relation to silicon and can release to it one more pair of electrons.

A result of this is a decrease in the polarity of the Si-Br bonds (Note: The direction of charges in the coordination bond Si-Br is opposite to what it must be in the ordinary valency bond between silicon and bromine) and a decrease in the relative weight of the ionic state which must be reflected adversely on the capacity of  $\text{SiBr}_4$  for bromine exchange.

- 3 -

SECRET

SECRET

**SECRET**

SECRET

50X1-HUM

Verification of the correctness of the hypothesis worked out for the influence of the partially double character of the Si-Br bond on the process of exchange of bromine in silicon tetrabromide is provided by the data of Brezhneva, Roginskiy, and Shilinskiy (3) on the virtually complete absence of exchange of bromine between aluminum bromide and those organic bromine derivatives in which the bromine is attached directly to the carbon atoms of the benzene ring. In these compounds, the C-Br bond is of partially double character (9), as distinguished from the alkyl derivatives, in which the C-Br bond is single, and which easily exchange their bromine with aluminum bromide (Note: Here it ought to be noted that the dipole moment of bromobenzene (1.52) is lower than the dipole moments of many monobromoalkyls).

Steric factors, which condition the value of the coordination number of the central atom of bromides, must also exert a large influence. The most probable coordination number for the addition of bromine on the part of a molecule of silicon tetrabromide is equal to 4, in which case a packing of maximum density results.

The ionic radius of silicon, found by Goldschmidt using X-rays, measurements, equal to 0.39A, and, calculated by Pauling from wave mechanics equations, 0.41A. The radius of bromine, correspondingly, is 1.96 and 1.95A. The relation between the radii of these ions, from the data of Goldschmidt, is equal to 0.199, and, from the data of Pauling, 0.21. This ratio is the most advantageous for the formation of a compound with the coordination number 4, since theoretically the tetrahedron formed will possess the densest packing when the ratio of the radii is 0.22 (10).

In carbon tetrabromide, the carbon has a radius which is somewhat shorter than it should be for dense packing with a coordination number of 4 and, therefore, carbon tetrabromide can undergo thermal dissociation, which probably determines the possibility of exchange with bromine.

Passing from silicon tetrabromide to bromides of elements of the carbon subgroup with larger ionic radii, the exchange proceeds as a result of the formation of complex compounds with a coordination number greater than 4 by bromides of these elements. Therefore, the tetrabromide of tin easily exchanges its bromine with free bromine.

## BIBLIOGRAPHY

1. A. I. Brodskiy, Izv AN SSSR, OKhN, 3 (1949).
2. G. P. Miklukhin, DAN 70, 437 (1950).
3. N. Ye. Brezhneva, S. Z. Roginskiy, and A. I. Shilinskiy, ZhFKh, Vol IX, 296 (1937).
4. A. A. Grinberg, Uspe Khim, Vol IX, 771 (1940).
5. J. Hodges and A. Miceli, Journ Chem Phys, Vol IX, 725 (1941).
6. V. S. Plotnikov, O slozhnykh soyedineniyakh khloristogo i bromistogo alyuminiya (On the Complex Compounds of Aluminum Chloride and Bromide), Kiev, 1902.
7. Ya. A. Kialkov, Doslikzhennya v galuzi kompleksnykh spoluk galogenidiv alyuminivu i poligalogenidiv, (Investigations in the Field of Complex Compounds of Aluminum Halides and Polyhalides) Acad Sci, Ukrainian SSR, Kiev, 1947.
8. I. A. Sheka, ZhFKh, Vol XVI, 99 (1942).
9. A. I. Kiprianov, Elektronnaya teoriya v organicheskoy khimii (Electronic Theory in organic Chemistry), 1949, p 90.

- 4 -

SECRET

**SECRET**

**SECRET**

SECRET

50X1-HUM

10. A. A. Grinberg, Vvedeniye v khimiyu kompleksnykh soyedineniy (Introduction to the Chemistry of Complex compounds), 1945, p 292.

Table 1. Systems: Bromine-Bromides of Carbon, Silicon, and Tin

<u>Components of Reaction</u>	<u>Physical State</u>	<u>Temp in °C</u>	<u>Duration of Interaction in Min</u>	<u>Activity</u>	
				<u>Bromium Compounds</u>	<u>Bromine</u>
$\text{CBr}_4\text{-Br}_2$	Liquid	20	180	10	180
$\text{CBr}_4\text{-Br}_2$	Homogeneous liquid and vapor	100	180	32	308
$\text{SiBr}_4\text{-Br}_2$	Liquid	20	240	0	176
$\text{SiBr}_4\text{-Br}_2$	Homogeneous liquid and vapor	100	240	0	419
$\text{SnBr}_4\text{-Br}_2$	Liquid	20	60	64	60

Table 2. Systems: Aluminum Bromide-Tetrabromides of Carbon and Tin

<u>System</u>	<u>Physical State</u>	<u>Temp in °C</u>	<u>Activity of Bromine</u>	
			<u>from <math>\text{RBr}_4</math></u>	<u>from <math>\text{AlBr}_3</math></u>
$\text{CBr}_4\text{-AlBr}_3$	Liquid	50	203	211
$\text{CBr}_4\text{-AlBr}_3$	Liquid	95	324	313
$\text{SiBr}_4\text{-AlBr}_3$	Liquid	100	3	151

- E N D -

- 5 -

SECRET

**SECRET**